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THE CRYSTAL AND MOLECULAR STRUCTURE OF 5,5-DIPHENYLOCTAFLUOROGERMANTHRENE, $(C_6H_5)_2GeC_{12}F_8$

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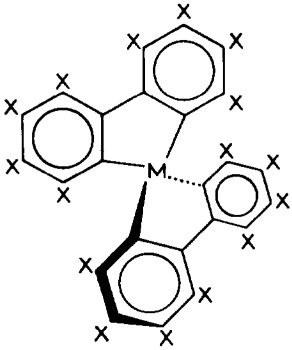
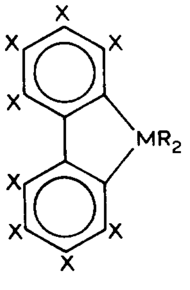
Summary

F---F steric interactions between the two 6,6′-fluorines of the C_6F_4 rings in $C_{12}F_8Ge(C_6H_5)_2$ cause quite severe distortions in the molecule as these two fluorine atoms are forced to within 2.419 Å of each other (Van der Waals distance $\simeq$ 2.7 Å). Crystal data: $C_{12}F_8Ge(C_6H_5)_2$, M_r 522.89, $C2/c$, a 29.065(2), b 8.066(2), c 23.000(3) Å, β 129.85°, U 4139.63 Å^3, $Z = 8$, D_x 1.678 Mg m^{-3}, Mo-K_α, λ 0.7107 Å, μ 15.58 cm^{-1}, $F(000) = 2064$, T 293 K, $R = 0.044$ for 2264 reflections with $I > 3\sigma(I)$; $\Delta\rho$ ± 0.5 e$^-$.

Hydrogen-substituted heterocycles such as I and II have been well known for many years, but a study of scale models suggested that the slightly larger size of fluorine (Van der Waals radius 1.35 Å) relative to that of hydrogen (1.2 Å) would render the perfluoro analogues unstable due to adverse steric interaction between the



(I)



(II)

(X = H or F)
(R = alkyl ; aryl ; C_5H_5 or no group)

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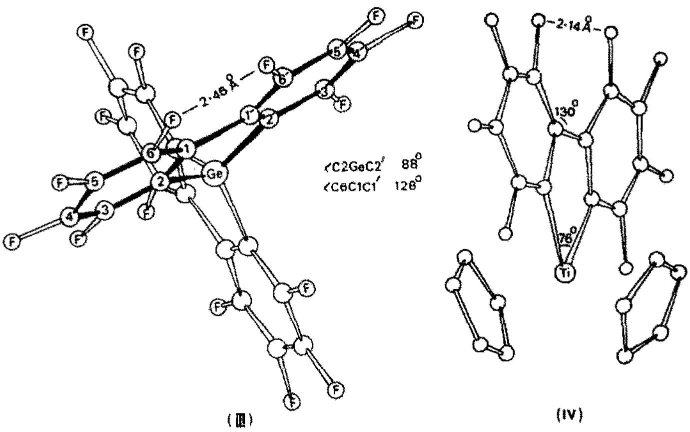

(III) (IV)

Fig. 1. The structures [3] of $Ge(C_{12}F_8)_2$ and $(C_5H_5)_2TiC_{12}F_8$ showing the in-plane bending of the octafluorobiphenyl groups and the close approach of the 6,6'-fluorine atoms.

6,6'-fluorines. Furthermore it has been stated [1] that fluorine atoms have an oblate spheroidal structure in which the shortest Van der Waals radius of 1.35 Å is that directly opposite the atom bonded to fluorine; at other angles the radius is larger and hence, because of their "side-on" approach, the 6,6'-fluorine atoms in I and II will interact even more adversely than suggested by spherical atomic models. For some unknown reason the first four attempts to synthesise $Ge(C_{12}F_8)_2$ (I) ($M =$ Ge, $X =$ F) via the reaction

$$2,2'\text{-}Li_2C_{12}F_8 + GeCl_4 \xrightarrow[\text{hexane}]{\text{ether-}} Ge(C_{12}F_8)_2$$

failed, apparently in agreement with the theoretical expectation of adverse steric interactions. However, it proved possible to make the compound at the fifth and subsequent attempts. The spiro-heterocycle proved to be so thermally stable [2] that it could even be obtained via a "direct synthesis" carried out at 390°C in an evacuated, sealed tube:

$$2,2'\text{-}I_2C_{12}F_8 + Ge \rightarrow Ge(C_{12}F_8)_2 + GeI_4$$

Some years ago the X-ray structures of $Ge(C_{12}F_8)_2$ and $(C_5H_5)_2TiC_{12}F_8$ (II) ($R = \pi\text{-}C_5H_5$, $M =$ Ti) were studied using photographic methods [3] which showed first of all that the basic distortions in the molecules (Fig. 1) mainly took the form of in-plane bending about the C–C bond joining the two C_6F_4 rings in the $C_{12}F_8$ groups, and also that the 6,6'-fluorine atoms were considerably less than 2.7 Å apart. However, because of the relatively crude photographic data used the finer details of the distortions were not resolved. We now report a diffractometric study on the structure of the related molecule, 5,5-diphenyl-octafluorogermanthrene (II) ($M =$ Ge, $X =$ F, $R = C_6H_5$) which also shows considerable steric interaction between the 6,6'-fluorine atoms. Dr. S.C. Cohen kindly provided us with single crystals grown from ethyl alcohol.

Experimental

The title compound was prepared by adding n-butyllithium (12.5 ml of a hexane solution) to 4.56 g of 2,2'-dibromooctafluorobiphenyl in 75 ml of ether held at

−78°C under nitrogen. After stirring for 2 h, diphenylgermanium dichloride (2.98 g) was added, the cold bath removed and stirring continued for a further 3 h once the mixture had attained room temperature. This resulted in a yellow solution and a white precipitate of lithium chloride; after filtering off the LiCl the solvent was removed to give a yellow-brown solid which was recrystallized from ethanol and further purified by vacuum sublimation at 120–130°C (10^{-4} mmHg) to give colourless needles of 5,5-diphenyloctafluorogermanthrene: yield 2.6 g (50%), m.p. 138.5–140.5°C (Found: C, 55.0; H, 2.1; F, 28.9. $C_{24}H_{10}F_8Ge$ calcd.: C, 55.1; H, 1.9; F, 29.1%). Infrared spectrum (cm^{-1}); 1626w, 1603m, 1580 wsh, 1484s, 1464s, 1429s, 1399ssh, 1379 s, 1350m, 1333m, 1302s, 1285m, 1258w, 1252m, 1238w, 1188w, 1160w, 1094s, 1059sbr, 1031s, 1028ssh, 998m, 921m, 823m, 786w, 733s, 724m, 706s, 693s, 678w, 640w, 595w.

The chosen crystal (0.13 × 0.12 × 0.20 mm) was grown from ethanol and mounted about the *b* axis on a fibre. Data were collected on a Stöe Stadi two-circle

TABLE 1

ATOMIC COORDINATES ($\times 10^4$)

Atom	*x*	*y*	*z*
Ge	3957.5(2)	4053.5(6)	5341.1(3)
C(1)	3414(2)	5903(5)	4834(3)
C(2)	3025(2)	6044(6)	4050(3)
C(3)	2362(3)	2416(7)	1298(3)
C(4)	2639(3)	8602(7)	4121(4)
C(5)	3010(3)	8458(7)	4887(4)
C(6)	3407(3)	7124(7)	5245(3)
C(7)	3807(3)	2743(6)	5912(2)
C(8)	3314(3)	2971(7)	5844(3)
C(9)	3202(3)	2006(8)	6240(4)
C(10)	3596(4)	805(9)	6726(3)
C(11)	4088(4)	543(9)	6796(4)
C(12)	4211(3)	1485(9)	6401(3)
C(13)	4056(2)	2719(5)	4719(2)
C(14)	3619(3)	1889(6)	4063(3)
C(15)	3755(3)	1050(6)	3564(3)
C(16)	4322(3)	1045(6)	3924(3)
C(17)	4769(3)	1868(6)	4588(3)
C(18)	4652(2)	2701(5)	5006(2)
C(19)	5081(2)	3642(5)	5730(3)
C(20)	5694(3)	3731(6)	6190(3)
C(21)	6031(3)	4670(7)	6848(3)
C(22)	5760(3)	5555(7)	7051(3)
C(23)	5156(3)	5474(6)	6615(3)
C(24)	4811(2)	4526(5)	5966(2)
F(14)	3043(1)	1941(4)	3780(2)
F(15)	3317(2)	254(4)	3010(2)
F(16)	4456(2)	246(4)	3543(2)
F(17)	5312(2)	1810(4)	4779(2)
F(20)	6012(2)	2847(5)	6062(2)
F(21)	6627(2)	4718(5)	7273(2)
F(22)	6089(2)	6509(5)	7684(2)
F(23)	4881(2)	6355(5)	6822(2)

diffractometer allowing the measurement of 3549 reflections of which 2264 had $I > 3\sigma(I)$ and were classed as observed; no absorption corrections were made as the crystal was very small and had a relatively low absorption coefficient. The germanium atom was found by a Patterson map and the position of all other atoms except three of the hydrogens were obtained from successive difference syntheses. The remaining three hydrogen atoms were placed in calculated positions and none of the ten was refined; all non-hydrogen atoms were refined anisotropically. In the final cycle of refinement $R = 0.044$; $w = 4.1758/[\sigma^2(F) + 0.000194F^2]$; $\Delta/\sigma < 0.02$; $\Delta\rho$ excursions $= \pm 0.5$ e$^-$. The structure solution and refinement used the SHELX-76 package [4]; geometry calculations and drawings were performed with XRAY72 [5] and ORTEP [6], respectively. Crystal data: $C_{12}F_8Ge(C_6H_5)_2$, M_r 522.89, $C2/c$, a 29.065(2), b 8.066(2), c 23.000(3) Å, β 129.85°, U 4139.63 Å^3, $Z = 8$, D_x 1.678 Mg m^{-3}, Mo-K_α, λ 0.7107 Å, μ 15.58 cm^{-1}, $F(000) = 2064$, T 293 K, $R = 0.044$ for 2264 observed reflections with $I > 3\sigma(I)$.

Discussion

Table 1 quotes the atomic coordinates from which the bond lengths and bond angles of Fig. 3 were calculated. Table 2 gives the deviations from the mean plane of the atoms in each ring system; for example, the C_6H_5 rings are virtually planar, the twist between the two phenyl planes being 66.2° and the angle C(1)GeC(7) 112.3°. The atoms in the five-membered ring are also essentially in the same plane; the very acute C(13)GeC(24) angle of 86.1° makes the coordination about germanium considerably distorted from the usual tetrahedral array. The constraints imposed by the other angles in this ring (varying from 112–114.5°) combine to make angles

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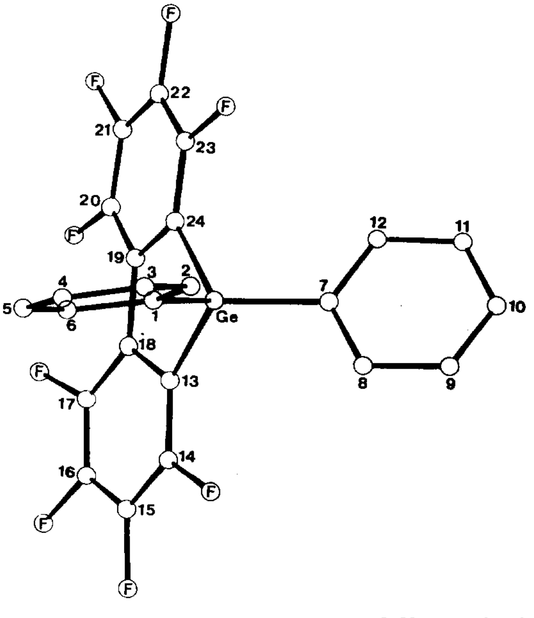

Fig. 2. ORTEP drawing of the $C_{12}F_8Ge(C_6H_5)_2$ molecule.

TABLE 2

LEAST-SQUARES PLANE THROUGH THE VARIOUS RINGS IN 5,5-DIPHENYLOCTAFLUOROGERMANTHRENE ($\sigma = 0.0002–0.0004$ Å), AND ANGLES BETWEEN THE RING PLANES (°)

Ring	Atom	Deviation from mean plane (Å)
GeC(13)C(18)C(19)C(24)	Ge	+0.020
(Ring 1)	C(13)	−0.005
	C(18)	−0.017
	C(19)	+0.040
	C(24)	−0.038
C(1)–C(6)	C(1)	−0.001
(Ring 2)	C(2)	−0.004
	C(3)	+0.001
	C(4)	+0.008
	C(5)	−0.014
	C(6)	+0.010
C(7)–C(12)	C(7)	+0.004
(Ring 3)	C(8)	+0.002
	C(9)	−0.008
	C(10)	+0.009
	C(11)	−0.003
	C(12)	−0.004
C(13)–C(18)	C(13)	−0.009
(Ring 4)	C(14)	+0.002
	C(15)	+0.004
	C(16)	−0.002
	C(17)	−0.005
	C(18)	+0.010
	F(14)	−0.046
	F(15)	−0.005
	F(16)	−0.005
	F(17)	−0.045
C(19)–C(24)	C(19)	−0.012
(Ring 5)	C(20)	0.000
	C(21)	+0.011
	C(22)	−0.010
	C(23)	−0.002
	C(24)	+0.013
	F(20)	+0.082
	F(21)	+0.016
	F(22)	−0.036
	F(23)	−0.011

Ring–Ring	Angle (°)
2–3	66.2
2–4	55.8
3–4	80.8
2–5	49.5
3–5	82.4
4–5	7.74

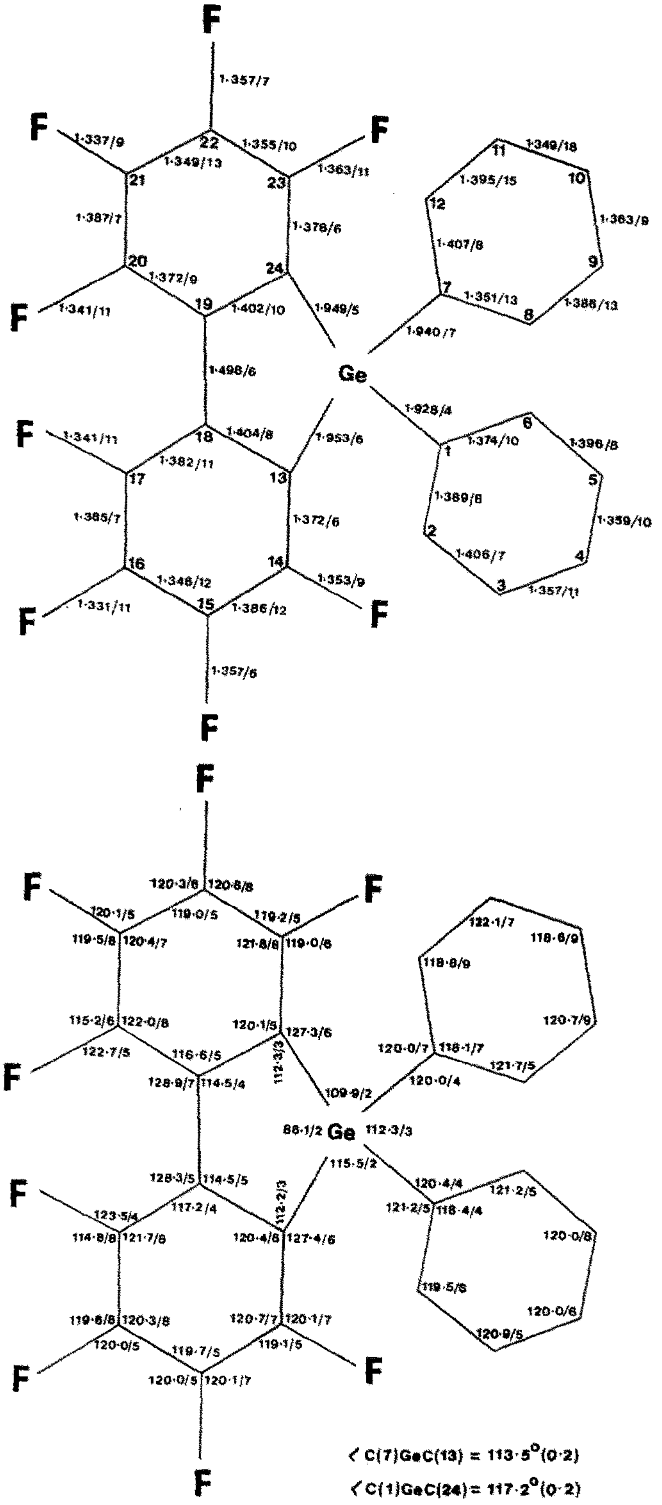

Fig. 3. Bond lengths (Å), bond angles (°), atom numbering and ring numbering in $C_{12}F_8Ge(C_6H_5)_2$; the estimated standard deviations are given in parentheses.

GeC(13)C(14) and GeC(24)C(23) larger than the sp^2 value (127.4 and 127.3°, respectively). An ORTEP drawing of the molecule is shown in Fig. 2 from which it is possible to see some of the distortions discussed below.

The main interest in the structure lies in the octafluorobiphenylene group. The two fluorines F(17) and F(20) are forced to be only 2.419(5) Å apart by the conformation of the molecule, which is much less than twice the normally accepted fluorine Van der Waals radius of 1.35 Å. There are several points of interest arising from this adverse steric interaction as summarized below.

(1) As in the molecules III and IV of Fig. 1 there is in-plane bending about the inter-ring C–C bond to give angles C(17)C(18)C(19) and C(18)C(19)C(20) the values 128.3(0.5) and 128.9(0.7)°, respectively, which has the secondary effect of making the other two angles about C(18) and C(19), considerably less than the sp^2 value of 120°.

(2) Although this in-plane bending evidences severe strain in this part of the molecule, it is of interest to note that the inter-ring bond, C(18)–C(19), has what appears to be a normal value [7] of 1.498(6) Å.

(3) Furthermore, the F(17)–C(17) and F(20)–C(20) bonds are identical, within experimental error, to the other six C–F bonds in the molecule. Hence it would appear that the F- - -F steric interaction is not manifested as detectable changes in the lengths of any of the neighbouring bonds.

(4) Somewhat surprisingly, the angles C(18)C(17)F(17) and C(19)C(20)F(20) are only opened up by about 3 from 120°. However, angles F(17)C(17)C(16) and F(20)C(20)C(21) are reduced to 115° which brings fluorines F(16),F(17) and F(20),F(21) slightly closer together (2.607(4) and 2.617(5) Å, respectively) than the Van der Waals distance of 2.7 Å but does not open the angles C(17)C(16)F(16) and C(20)C(21)F(21), which are within experimental error of 120°.

(5) Besides causing in-plane bending across the C_6F_4 rings, the F- - -F interaction also introduces a slight twist of 7.74° between the two rings, an effect which was not noticed in the earlier work on III and IV.

(6) The two *para* C–F bonds C(15)–F(15) and C(22)–F(22) make angles of 6.47 and 7.05°, respectively, with the inner-ring bond C(18)–C(19) and 13.33° with each other. A scale drawing shows that these angles are due only to the in-plane bending discussed in (1) above.

As described in the Introduction the oblate-spheroidal shape of the fluorine atoms will make the Van der Waals contact between the non-end on approach of F(17) and F(20) greater than the normally accepted value of about 2.7 Å thus increasing the steric congestion even further than originally expected, which probably accounts for the very marked distortions noted in this molecule. The other F- - -F non-bonded contacts in the molecule are: F(14)–F(15), 2.726(8); F(15)–F(16), 2.695(8); F(21)–F(22), 2.706(9) and F(22)–F(23), 2.712(7) Å. We plan to study other molecules containing the 2,2′-$C_{12}F_8$ group to detect how the other substituent groups in the molecules enhance or relieve the F- - -F interactions.

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